THE PREPARATION OF A SOLID RHENIDE

by

Justo B. Bravo
B. S. Ch. E., Adamson University
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Advisory Committee:

Redacted Signature

Chairman

Redacted Signature

Redacted Signature

Redacted Signature

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I. INTRODUCTION

Since the discovery of rhenium in 1925, a considerable body of information has been accumulated on the chemistry of this element. In the periodic classification of the elements, rhenium is grouped with manganese and technetium in arrangements based on the atomic number of the elements, the number of shells in the atoms, and the type and number of electrons in the incompleted shells. In the ordinary periodic arrangements these elements are arranged in subgroup A of the seventh group, whereas fluorine, chlorine, bromine, iodine and astatine are placed in subgroup B.

The valences of manganese range from +2 to +7 in its ordinary compounds. The valences of the members of the halogen subgroup range from -1, which is common to all, to +7, which is exhibited by chlorine and iodine. If rhenium follows manganese in its valences, one might expect the lowest valence state to be +2 and the highest valence state to be +7. If rhenium follows the halogen subgroup in its valences the lowest valence state should be -1.

The most characteristic valence state of rhenium is +7 and is exhibited in several of its most important and most stable compounds, such as the heptoxide, Re_2O_7, and perrhenic acid, $HReO_4$, and its salts. In compounds like the hexafluoride, ReF_6, the trioxide, ReO_3, the oxytetrachloride, $ReOCl_4$, and the oxythiocyanate,

$ReO(CNS)_4$, the valence state of rhenium is +6. A state of +5 is shown by the element in a few compounds, e.g., the pentachloride, $ReCl_5$, whereas in the dioxide, the tetrafluoride, and the double halides of the type K_2ReCl_6, the element exhibits a +4 oxidation state. The +3 state is shown in the trihalides, the double salts like $RbReCl_4$, as well as in trimethyl rhenium. It has been shown that in glacial acetic acid the trichloride has a molecular weight corresponding to the formula Re_3Cl_6, and Geilmann and Wrigge represent the compound as consisting of two rhenium tetrachloride tetrahedra in which two chlorine atoms are shared by the rhenium atoms.[1]

It has been claimed that oxides of both unipositive and dipositive rhenium can be obtained by reducing perrhenic acid with zinc and cadmium, respectively, in the presence of hydrochloric acid.[2] When reduced by means of the Jones reductor (zinc amalgam), perrhenic acid behaves analogously to the halogen oxy-acids, the +7 rhenium being converted to uninegative rhenium (i.e., to the rhenide ion).[3]

The investigation reported herein was undertaken to prepare a solid rhenide compound. The specific objectives were (a) to establish the method of preparation and (b) to determine the structure of the compound produced.

II. HISTORICAL REVIEW

Uninegative rhenium was first obtained by Lundell and Knowles[3] in 1937. A study of the behavior of rhenium when dilute solutions of potassium perrhenate were acidified with sulfuric acid, cooled, and passed through a Jones reductor from which air had been carefully excluded, indicated that rhenium forms a compound in which it has a valence state of -1. The reduced solutions were found to have reducing power corresponding to eight equivalents for each atom of rhenium;

$$Re^- + 4H_2O = ReO_4^- + 8H^+ + 8e^-$$

The oxidation number was established by titration to perrhenate by means of potassium permanganate and other oxidizing agents. The existence of uninegative rhenium was confirmed by Tomiček and Tomiček,[4] and by Lingane.[5] The name rhenide was given to this oxidation state.

Lundell and Knowles[3] discovered that solutions of rhenide ion in 1.8 N sulfuric acid were slowly oxidized and acquired a straw-yellow color when they were warmed to about 50°C for thirty to sixty minutes in the absence of oxygen. These investigators passed pure carbon dioxide through the solution during the warming and discovered that the effluent gas contained a volatile sulfur compound which very likely was sulfur dioxide. Tomiček and Tomiček[4] have reported the evolution of hydrogen sulfide, as well as sulfur dioxide in this reaction.

In the reduction of perrhenate ion at the dropping mercury electrode, Lingane[5] obtained polarograms of various concentrations of perrhenate ion in 2 N potassium chloride solution as supporting electrolyte. With the smallest concentration of perrhenate ion a well defined wave was obtained whose half wave potential was -1.41 v. vs. the saturated calomel electrode, corresponding to the reduction to the rhenide ion. In another investigation, Lingane[6] described a zinc reductor in which reductions could be performed conveniently air-free and at controlled temperatures. He confirmed the formation of -1 rhenium in reductions carried out in dilute sulfuric and perchloric acid solutions. Polarograms of the rhenide solutions in 1 to 2 N sulfuric acid at 0°C displayed three anodic waves, whose half wave potentials were (α) -0.54 v., (β) -0.34 v., and (γ) -0.07 v. vs. the saturated calomel electrode. A similar polarogram was found in 1 N perchloric acid except that (a) the β wave was resolved into two separate waves, β' and β'', whose half wave potentials were -0.42 and -0.26 v., respectively and (b) the half wave potential of the γ wave was about 0.1 v. more positive than in sulfuric acid medium. From the ratio of the various wave heights it was concluded that the α wave resulted from the oxidation of uninegative rhenium to the +2 state, the β' wave from oxidation of the +2 to the +3 state, the β''

wave from conversion of the +3 to the +5 state and the γ wave from complete oxidation of the latter to the +7 state (ReO_4^-). These conclusions have been confirmed by amperometric titrations of the reduced solutions with ceric ion. Evidence was also presented which indicated that the reversible potential of the reaction, $Re^{+2} + 3e^- = Re^{-1}$ was equal to or slightly more negative than -0.54 v. vs. the saturated calomel electrode in dilute sulfuric and perchloric acid solutions at 0°C. Partially oxidized solutions obtained by warming dilute sulfuric acid solutions of -1 rhenium to about 50°C for an hour in the absence of oxygen showed an average oxidation state of +1. However, the polarogram of such a solution indicated that the rhenium was not actually present in the +1 state, but as a mixture of rhenide and higher states in proportions that were equivalent to an average oxidation state of +1.

Geyer[7] studied the polarographic reduction of perrhenate ion in neutral, alkaline, and acid solution. Six steps were observed at the following potential values: (1) -0.9 to -1.5 v., (2) -1.3 to -1.7 v., (3) 0.0 to 0.3 v., (4) -0.5 to 0.9 v., (5) +0.4 to +0.1 v., (6) -0.1 to +0.3 v. In alkaline, neutral, and very weak acid solutions, steps (1) and (2) were obtained: ReO_4^- $\underline{\underline{(1)}}$ Re $\underline{\underline{(2)}}$ Re^-; for normal acidity, steps (3) and (4) were found: Re^{+7} $\underline{\underline{(3)}}$ Re $\underline{\underline{(4)}}$ Re^-; for high acidity, these were found:

Re^{+7} (5) Re^{+4} (6) Re (4) Re^{-}.

The existence of -1 rhenium raised the interesting question of its electronic configuration. In the rhenium atom itself the first four quantum levels are completely filled and the configuration of the outer fifth and sixth levels is $5s^2 5p^6 5d^6 6s^2$. The addition of an electron to form -1 rhenium could lead to various configurations. Lingane[6] in 1942 suggested the following possible structures:

A $5s^2 5p^6 5d^6 6s^2$

B $5s^2 5p^6 6s^2 6p^6$

It is significant that negative oxidation states of all other elements involve the formation of the stable s^2p^6 octets, and on this basis one is inclined to assign structure B to -1 rhenium. The promotion of all of the 5d electrons is in accord with the marked instability and strong reducing character of -1 rhenium.

However, Pauling[8] in 1947 proposed for the rhenide ion a coplanar square type of binding such as shown by the isoelectronic +2 platinum. Accordingly, it was suggested that in aqueous acid solution a hydrated complex ion of formula, $[Re(H_2O)_4]^-$ may exist, which involves the dsp^2 type of binding shown below and derived from structure A.

	5d	6s	6p
Re atom - - - - - - - -	⊙⊙⊙⊙⊙	⊙	⊙⊙⊙
-1 rhenium - - - - - -	⊙⊙⊙⊙⊙	⊙	⊙⊙⊙
-1 rhenium complex - -	⊙⊙⊙⊙	○	⊙⊙⊙
		dsp^2	

Which theoretical assumption is correct, or whether either is, remains to be proved. If it should be demonstrated that the rhenide forms the coordination complex of the type mentioned it would lend considerable support to Pauling's proposal.

Maun and Davidson[9] prepared rhenide solutions by passing 0.001 F perrhenic acid in 4 F hydrochloric acid through a Jones reductor. These investigators found out that reduction was incomplete with higher concentrations of rhenium. They claimed that the -1 rhenium was completely oxidized to perrhenate by cerium(IV) sulfate or potassium iodate, and largely oxidized by iodine. Highly colored oxidation states were formed when the solutions containing rhenide ion were treated with copper(II) sulfate, perrhenate, or oxygen. An attempt to prepare a solid compound of -1 rhenium by reduction of K_2ReCl_6 by potassium metal gave only rhenium metal. When the rhenide solutions were concentrated by evaporation with the use of a mechanical pump, they showed a decrease in the amount of reducing power in the enriched product.

In studies conducted by Rulfs and Elving,[10] polarograms were obtained which gave five distinct anodic waves generally similar to those found by Lingane.[6] Results from amperometric oxidation of rhenide were in agreement with Lingane's conclusion that the +1 state

obtained by warming a rhenide solution[3] actually consisted of a mixture of rhenium species. Furthermore, Rulfs and Elving showed that in 0.7 to 7.0 N sulfuric acid the maximum concentration of potassium perrhenate which could be quantitatively reduced to the rhenide state in a Jones reductor was about 0.83 mM, whereas a rhenide concentration of at least 1.3 mM was attainable in 1.2 N hydrochloric acid and the latter figure could be raised to 2.6 mM by the addition of pyridinium chloride to the hydrochloric acid solutions prior to reduction. Addition of thallium(I) chloride to a solution 1 mM in rhenium in 2.4 N hydrochloric acid yielded no thallium(I) rhenide.[11]

III. EXPERIMENTAL

A. Materials

The materials important in the preparation of solid rhenide are described below.

Potassium perrhenate obtained from the University of Tennessee and of 99.8 per cent purity was used without further purification. The potassium sticks were obtained from Baker and Adamson. Anhydrous ethyl ether was produced by drying special drum ether from Carbide and Carbon Chemicals over sodium.

Ninety-eight per cent Baker and Adamson isopropyl alcohol was fractionated over sodium (1 gram of sodium per liter of alcohol). Fractionation was carried out in a 110 cm. bead-packed column, and the distillate collected at a reflux ratio of about 8 within the temperature range of 81° to 82°C was retained. The system was freed from air by flushing with dry nitrogen and all fractionations were protected from air by means of a constant stream of dry nitrogen.

Eastman Kodak Co. white label ethylenediamine was used. Karl Fischer reagent was purchased with the water-in-methanol standard from Hartman-Leddon Co. The ethylenediamine used was recovered by distillation from potassium hydroxide sticks.

B. Analytical Methods

1. Determination of the water content of the ethylenediamine. The water content of the ethylenediamine was determined by titration with Karl Fischer reagent with the use of a water-in-methanol standard.[12] The reagent consisted of solutions No. 1 and 2. Solution No. 1, sulfur dioxide in pyridine, was added to solution No. 2, iodine in methanol, a day before the reagent was used. Several 10 ml. portions of the standard water-in-methanol were transferred to dry standard taper flasks and titrated with the Fischer reagent until a persistent iodine color appeared. Several 5 ml. portions of the ethylenediamine were transferred to dry standard taper flasks and 10 ml. of water-in-methanol standard was added to each sample. These were titrated with the reagent.

2. Measurement of reducing power of the rhenide compound. Standard 0.05 N potassium dichromate solution was prepared directly from the C. p. Baker's analyzed material. An approximately 0.05 N iron(II) sulfate solution was prepared from C. p. Mohr's salt.[13] This was standardized against the potassium dichromate each time before use. Two-tenths per cent diphenylamine sulfonic acid indicator was used.[14] Solutions were delivered from 10 ml. semi-micro burettes.

A sample of rhenide compound was prepared by

dissolving the weighed dried solid in 10 per cent potassium hydroxide solution and diluting to an exact volume. A measured aliquot portion of this sample was introduced into a flask containing a measured quantity of an excess of standard potassium dichromate solution in a considerable amount of 4 N sulfuric acid and the mixture was shaken. Then a known volume of standard iron(II) sulfate solution was added and the excess back titrated with potassium dichromate solution in the presence of 2 to 4 drops of diphenylamine sulfonic acid indicator to a purple endpoint. Since the indicator consumes a little oxidizing agent, an indicator correction was made, corresponding to approximately 0.06 ml. of the 0.05 N dichromate solution for each milliliter of the 0.2 per cent indicator used.

3. Rhenium analysis. When an acid solution of perrhenate is treated with thiocyanate and tin(II) chloride solutions a yellow color appears, which has been ascribed to the formation of $ReO(CNS)_4$.[15] This complex is extractable with ether and is fairly stable. Slight deviation from Beer's Law is shown by the ether solutions, but this may be due to the slight instability of the solutions rather than to true deviations.

The following procedure employed for the spectrophotometric determination of rhenium is a slight modification of that described by Sandell.[16] It differs

only in the use of tin(II) chloride in place of mercury for the preparation of the ether used for extraction purposes.

Special solutions.

Potassium thiocyanate. 20 per cent aqueous solution.

Tin(II) chloride. 35 grams of $SnCl_2.2H_2O$ was dissolved in 20 ml. of 1:1 hydrochloric acid and diluted to 100 ml. with distilled water.

Ether for extraction and dilution. To 100 ml. of ethyl ether in a separatory funnel the following were added: 25 ml. of 1:4 hydrochloric acid, 2 ml. of 20 per cent potassium thiocyanate solution, and 2 ml. of tin(II) chloride solution. The mixture was shaken vigorously for one minute and the aqueous acid solution was discarded, leaving peroxide-free ether.

Determination of rhenium.

A measured volume of the sample was digested with 2 ml. of 30 per cent hydrogen peroxide (Superoxol) and 5 ml. of 1:1 hydrochloric acid. Digestion was stopped after the excess hydrogen peroxide had been destroyed. The sample was then transferred to a 60 ml. separatory funnel containing approximately 10 mg. of iron as iron(III) chloride (3 ml. of about 0.2 N $FeCl_3$) and 25 ml. of 1:4 hydrochloric acid. Two milliliters of potassium thiocyanate solution and 1 ml. of tin(II) chloride solution

were added. The mixture was shaken and allowed to stand for five minutes, after which 20 ml. of the specially made ether was added. The mixture was shaken vigorously, the phases were allowed to separate, and the aqueous acid solution was run into another separatory funnel. The aqueous solution was extracted twice more with 15 ml. portions of ether. The final acid layer was discarded and the ether extracts were combined, shaken well with 10 ml. of 1:4 hydrochloric acid to remove iron and transferred to a 100 ml. volumetric flask. The solution was diluted to the mark with the specially prepared ether. The optical density of the ether solution was determined using a Beckman DU spectrophotometer at a wave length of 4320 Å and a slit width opening of 0.05 mm.

For the construction of a calibration curve a series of standard rhenium solutions were prepared, each containing a known weight of potassium perrhenate together with 5 ml. of 6 N sulfuric acid made up to 50 ml. with distilled water. Aliquot portions of these solutions were treated as described above, except that the digestion with hydrogen peroxide was omitted. The optical densities corresponding to the known number of micrograms of rhenium present per milliliter of the ethereal solutions were recorded. A typical calibration curve is shown in Figure A.

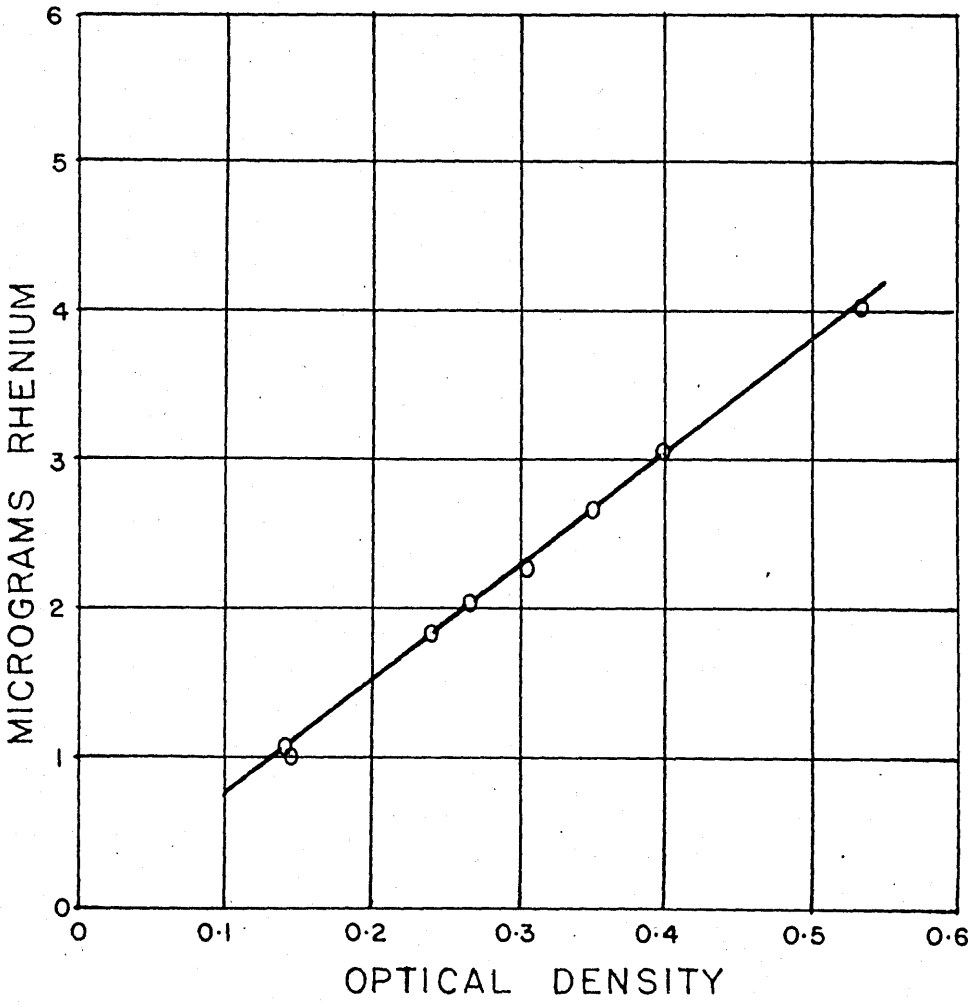

FIGURE A – STANDARD CALIBRATION CURVE FOR THE DETERMINATION OF RHENIUM. WAVE LENGTH 4320 Å.

4. Potassium analysis. Potassium was determined with the use of the Perkin-Elmer, Model 52-C Flame Photometer.[17] Both the standards and unknown were run at the maximum sensitivity wave length of 7665 Å for potassium using the internal standard method. The following standards, each containing 100 ppm of lithium as internal standard, were prepared from potassium perrhenate: 100 ppm, 80 ppm, 60 ppm, 40 ppm, 20 ppm, 10 ppm and 0 ppm of rhenium.

Weighed samples of solid rhenide (about 100 mg.) were dissolved in distilled water and digested with 5 ml. of 30 per cent hydrogen peroxide and 1 ml. of concentrated nitric acid until excess peroxide had been destroyed. Each sample was diluted exactly to an appropriate volume. Aliquots of each of these solutions were made up to 250 ml. with water and sufficient lithium standard to give 100 ppm of the latter element.

The determination were carried out as described in the Perkin-Elmer manual.[17] From the data obtained for the standards a calibration curve was constructed (Figure B).

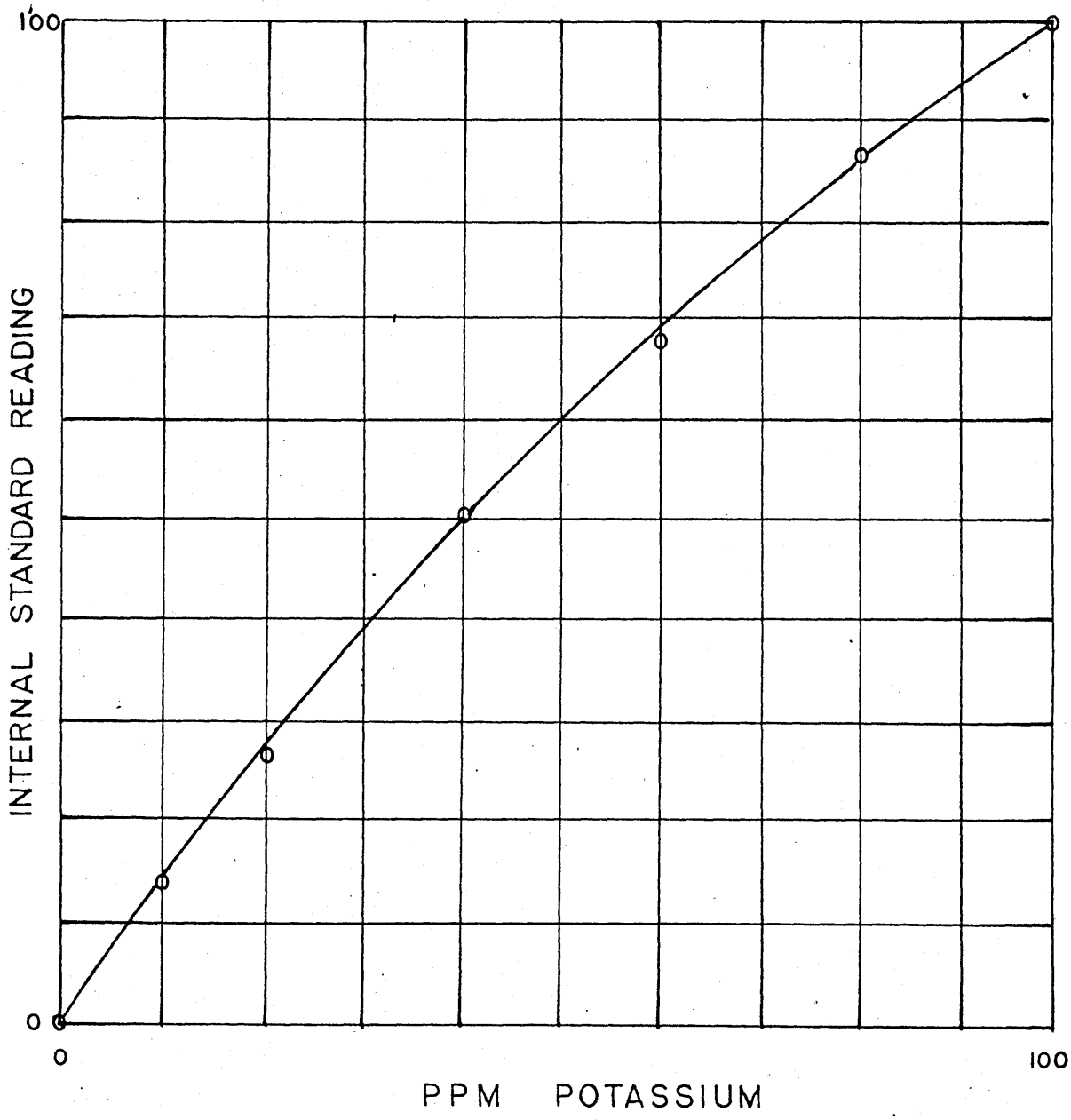

FIGURE B- STANDARD CALIBRATION CURVE FOR THE DETERMINATION OF POTASSIUM BY FLAME PHOTOMETRY.

WAVE LENGTH 7665 $\mathring{A}$.

C. The Reduction of Potassium Perrhenate.

1. Preliminary work. Several experiments were performed to check the observations of Lundell and Knowles[3] regarding the reduction of potassium perrhenate in a Jones reductor. Different concentrations of the salt, dissolved in either 1 N sulfuric acid or 1.2 to 2.5 N hydrochloric acid, were used in the various experiments. Fresh zinc amalgam was employed after each two reductions. In every run the amalgam was first activated with warm dilute sulfuric acid, followed by treatment with cooled distilled water. Then for at least 20 minutes, dry oxygen-free nitrogen was passed through the reductor, and the receiver containing an acidified oxidant was attached. The following order of introducing the solutions was followed:

1. 50 ml. of cold dilute acid,
2. Sample,
3. 50 ml. of cold dilute acid and
4. 100 ml. of cold water.

All solutions were freed from traces of air by boiling, and then were cooled in ice water in an oxygen-free atmosphere before use. An outer jacket was provided to cool the reductor during the course of the reduction.

The reducing power of the product was determined by titration with either standard permanganate or dichromate solution and the valence change of the rhenium

calculated on the basis of conversion to perrhenate by the oxidant. Typical values obtained for the valence state of rhenium in the product were -1.16, -0.80, -0.86, showing that rhenide ion was indeed formed. Inasmuch as use of the Jones reductor did not permit the formation of high concentrations of rhenide ion, experiments were designed to determine whether greater quantities could be produced.

Use of 3 per cent potassium amalgam as reducing agent in a specially constructed reductor was unsuccessful. Experiments with this reductor were carried out in an oxygen-free nitrogen atmosphere, with either pyridine or ethylenediamine being added to the aqueous potassium perrhenate solutions. It was hoped that these amines would stabilize any rhenide formed. However, large quantities of rhenium were converted to an amalgam and remained in the reductor. Also some pyridine was reduced to piperidine. In several of the reductions in the presence of ethylenediamine, the solution which came through the reductor contained appreciable quantities of rhenide ion. It was therefore decided to study the reduction of potassium perrhenate in ethylenediamine-water solutions with the use of potassium as reducing agent. It was hoped that the substitution of potassium metal for the amalgam would eliminate the conversion of perrhenate to rhenium metal.

2. Reduction of potassium perrhenate with potassium in ethylenediamine-water solutions. A simple apparatus was made, consisting of a large reaction tube having a ground glass cap. From the center of the cap a delivery tube extended to the bottom of the reaction tube and the side of the cap was provided with an outlet for nitrogen gas. The potassium was introduced by opening the reactor while the system was under a positive nitrogen pressure. The perrhenate sample was introduced through the delivery tube through which oxygen-free nitrogen also flowed. The gas was permitted to flow throughout the course of the reduction.

In a typical experiment, 30 to 40 ml. of a perrhenate solution of known concentration in ethylenediamine containing from 7 to 15 per cent water was introduced into the reaction tube to which had been added about 2 grams of metallic potassium. The products of reduction were a solid and a liquid and contained a considerable quantity of potassium hydroxide. The solid varied in color from white to gray to gray black. The liquid was filtered through a sintered-glass filter funnel and analyzed for rhenium content and reducing power. The reducing power was determined by addition of an aliquot of the liquid phase to an excess of an acidified (with sulfuric acid) solution of standard potassium dichromate and back-titration with standard iron(II) sulfate

solution. The experimental data are shown in Table I.

TABLE I

ANALYSIS OF LIQUIDS PRODUCED IN REDUCTION OF POTASSIUM PERRHENATE BY POTASSIUM IN ETHYLENEDIAMINE-WATER SOLUTIONS

$KReO_4$ orig. concn. mM	Reduction time, min.	Per cent water	Re content of aliquot, mg.	Ml. 0.1 N $K_2Cr_2O_7$ required	Final concn. mM	Valence number change; theo., 8
4.65	10	10	2.04	0.32	1.10	2.9
4.65	10	10	1.05	0.18	0.56	3.2
8.4	30	7	0.47	0.20	0.25	7.9
8.4	5	15	0.13	0.06	0.07	8.6
8.4	60	7	0.75	0.33	0.40	8.2

It is evident that most of the rhenium is left in the solid phase when conversion to rhenide in the liquid phase is practically complete. The solid phase always contained some metallic rhenium. The formation of the metallic rhenium was observed to take place to the greatest extent in experiments where original concentrations of the perrhenate in the sample were highest. Attention was next directed to the solid phase, and

experiments were designed to determine the conditions necessary for maximum conversion of perrhenate to solid rhenide. Various concentrations of potassium perrhenate in ethylenediamine-water solution were used. The weight of the potassium was also varied in the experiments, and three different water concentrations were used in the series of experiments. The time of reduction ranged from 2 minutes to 15 minutes and depended on the proportion of water to potassium.

Fifty milliliters of the sample containing potassium perrhenate was cooled in an ice bath to about 10°C. The apparatus described above was made air-free by means of a constant flow of nitrogen and the potassium, weighed under benzene, was introduced into the reaction tube. The perrhenate sample was then introduced into a funnel and permitted to drain through the delivery tube into the reaction tube containing a weighed quantity of potassium. When all the potassium had reacted, the mixture containing the solids was filtered through an ultrafine sintered-glass funnel, the solids washed with a few milliliters of pure ethylenediamine, and then dissolved in 12 ml. of distilled water. Ten milliliters of the solution was titrated for reducing power and a fraction of a milliliter was used for the spectrophotometric determination of rhenium. The procedures for the titration and spectrophotometric analysis have already been discussed (pp. 10-13).

TABLE II

ANALYSIS OF SOLIDS PRODUCED IN REDUCTION OF POTASSIUM PERRHENATE BY POTASSIUM IN ETHYLENEDIAMINE-WATER SOLUTIONS

Orig. concn. $KReO_4$, mM	Grams K per 50 ml. $KReO_4$ soln.	Per cent H_2O	Re content titrated, mg.	Ml. 0.1 N $K_2Cr_2O_7$ required	Valence number change; Theo., 8	Valence of Re
10	4.0	12	8.04	3.11	7.21	-0.21
5	2.5	11	11.68	4.43	7.07	-0.07
5	1.5	10	10.60	4.19	7.36	-0.36
5	1.0	12	7.68	2.97	7.21	-0.21
3	2.0	10	7.00	3.00	7.99	-0.99
3	2.0	10	8.22	3.43	7.78	-0.78
3	2.0	10	6.82	2.81	7.68	-0.68
3	1.9	10	5.80	2.48	7.96	-0.96
3	2.0	10	6.80	2.89	7.92	-0.92
3	2.0	10	7.20	2.97	7.70	-0.70

In Table II are shown data obtained from solids produced in a series of reductions of potassium perrhenate by metallic potassium in ethylenediamine-water solutions. With original concentrations of perrhenate of 5 mM and higher the solids produced contained some rhenium metal. When the solid was dissolved in water additional rhenium metal appeared to be formed, presumably as a result of reaction between unreacted perrhenate and rhenide ions. With a 3 mM perrhenate concentration initially, the reduction gave a white solid in which the rhenium was essentially in the rhenide state.

Additional experiments were carried out to establish the potassium and water requirements for optimum conversion of perrhenate to rhenide. The apparatus employed for the reductions is shown in Figure I. The reaction chamber was about 3.5 cm. in diameter and approximately 15 cm. high. Sampling bulbs A and B were inserted in the reaction chamber through ground glass joints. The nitrogen delivery tube extended close to the bottom of the reaction chamber in order that the gas would have a stirring effect on the reaction mixture. The presence at C of a large standard taper joint permitted the removal of the lower part of the reaction chamber for sampling purposes. An ultrafine fritted glass disk sealed into the bottom of the

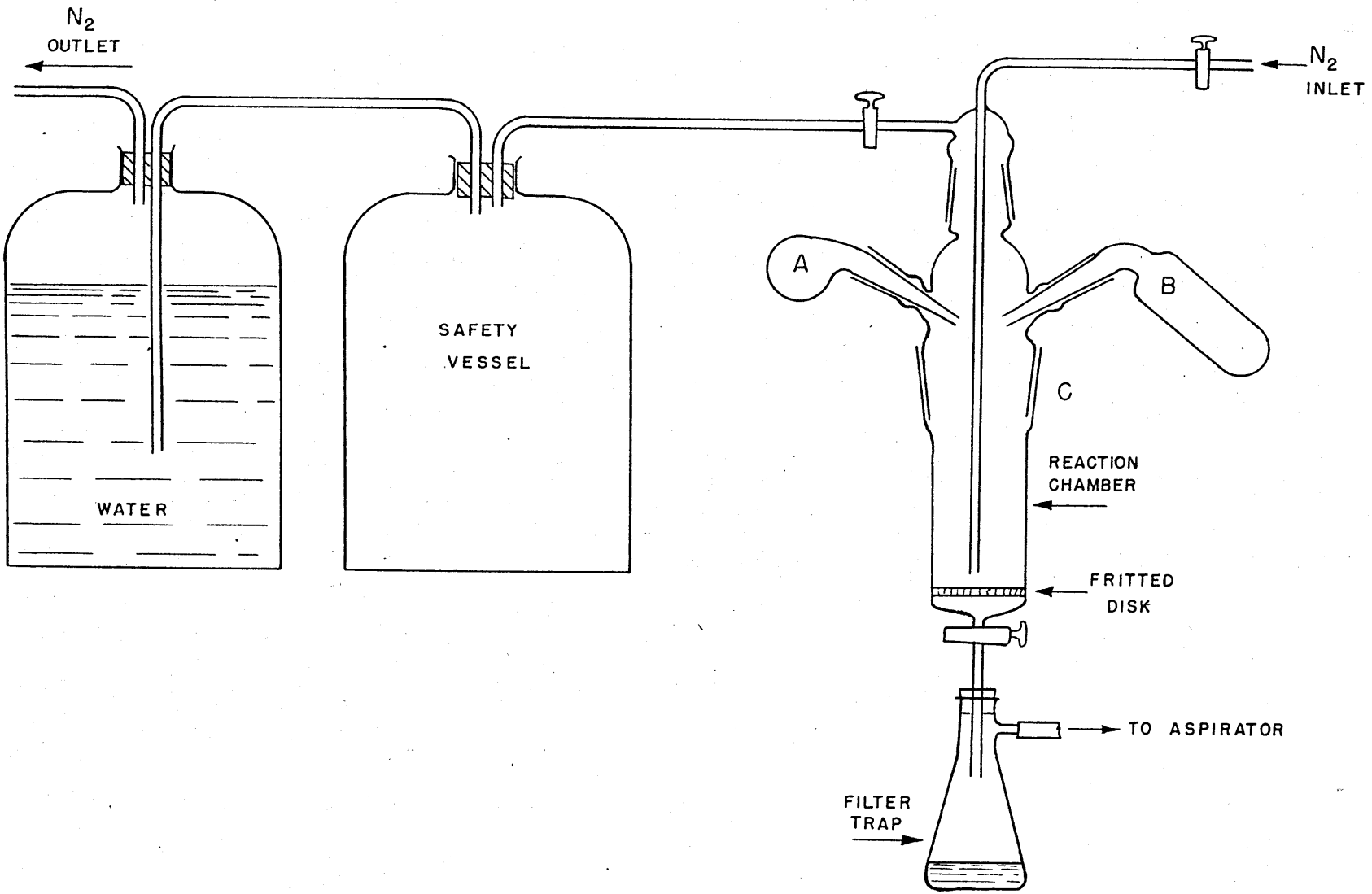

Figure 1 Apparatus for Reduction of Potassium Perrhenate Solution with Metallic Potassium.

reaction chamber served, after the removal of the solvent into the filter trap by means of an aspirator, to hold the insoluble white product formed in the reduction reactions.

Prior to each reduction the several pieces of the reaction chamber assembly were cleaned and dried in an oven at 110°C. The apparatus was then assembled except for the sampling bulbs. The openings for the bulbs were stoppered with standard taper plugs and dry oxygen-free nitrogen was passed through the system for at least 10 minutes to sweep out the air. The nitrogen was purified by successive passage through alkaline pyrogallol solution, chromium(II) sulfate solution, concentrated sulfuric acid, and finally a drying tower containing a mixture of calcium chloride, potassium hydroxide pellets and magnesium perchlorate. The sampling bulb A was then charged with a weighed quantity (2 or 4 grams) of Baker and Adamson potassium, which had been cut and weighed under benzene.

Bulb B was charged with 50 or 100 ml. of 3 mM potassium perrhenate solution in various mixtures of ethylenediamine and water. After the sampling bulbs had been connected with the reaction chamber, bulb A was rotated and the potassium metal dropped into the chamber. This was followed by the introduction of the perrhenate solution.

Usually from 2 to 10 minutes was required for complete reaction of the potassium, during which time the temperature of the reaction mixture rose to about 70°C. When the reaction was complete, the solid product was filtered by aspiration and twice washed with anhydrous ethyl ether, being stirred at the same time. After a final rinse with ether the solid was dried thoroughly by means of a stream of dry nitrogen and was then made up to volume with distilled water. Separate aliquots of the solution were analyzed for rhenium content and reducing power in terms of the number of equivalents of standard oxidizing agent (potassium dichromate) required to oxidize the rhenium to the perrhenate state.

It was found that conditions which give excellent conversion of the perrhenate to solid rhenide are as follows:

(1) Composition of solvent, 9.8 g. of water per 100 ml. of ethylenediamine-water solution.

(2) Initial concentration of potassium perrhenate, 3 mM.

(3) Potassium requirement, 4 grams per 100 ml. of solution.

(4) Initial temperature, about 25°C.

The results of typical experiments are given in Table III. It is seen that under optimum conditions more than 50 per cent of the initial perrhenate is converted to

TABLE III

REDUCTION OF POTASSIUM PERRHENATE

BY POTASSIUM IN ETHYLENEDIAMINE-WATER SOLUTIONS

(Concentration of $KReO_4$, 3 mM; 9.8 per cent H_2O)

Millimoles Re titrated	Ml. 0.1 N $K_2Cr_2O_7$ required	Valence number change; theoretical, 8	Total Re, mg.	Conversion to rhenide, per cent
0.0376	3.00	7.99	8.40	30.0[a,c]
0.0311	2.48	7.97	6.96	24.9[a,c]
0.0365	2.89	7.92	8.16	29.2[a,c]
0.0174	1.39	7.97	5.02	18.0[a,c]
0.0651	5.32	8.16	14.50	52.0[a]
0.0681	5.33	7.82	15.26	54.7[a]
0.1014	8.44	8.30	37.80	67.6[b]
0.1356	11.02	8.13	50.50	90.4[b]
0.1390	11.38	8.18	51.76	92.5[b]

[a] Fifty milliliters of perrhenate sample and 2.00 (± 0.05) g. of potassium were used in these experiments.

[b] One hundred milliliters of perrhenate sample and 4.00 (± 0.05) g. of potassium were used in these experiments.

[c] Initial reaction temperature 15°C.; all other experiments were carried out at an initial temperature of about 25°C.

solid rhenide. The solid contains about 0.5 per cent of rhenium. In almost every case, the filtrate possessed some reducing power, indicating that it contained rhenide.

3. Some properties of the white solid. In addition to rhenide, the white solid contained large quantities of potassium hydroxide, resulting from reaction between water and potassium metal. Treatment of an aqueous solution of the solid with a solution of thallium(I) nitrate resulted in the precipitation of a white solid. This solid presumably is thallium(I) rhenide, inasmuch as thallium(I) hydroxide is soluble. Unfortunately the precipitate proved to be unstable and soon became converted to a black material. The black material proved to be metallic thallium; perrhenate was identified in the solution.

D. The Separation of Potassium Rhenide.

1. Preliminary work. The white solid mixture of rhenide and potassium hydroxide produced by the method previously discussed (p. 25), was subjected to liquid ammonia extraction. About 100 ml. of liquid ammonia was condensed in the reaction chamber of the apparatus shown in Figure I. The ammonia, maintained at its boiling point to provide stirring action, was kept in contact with the mixture for about an hour and was then filtered by means of suction. The ammonia filtrate was allowed to evaporate to dryness and was then analyzed for rhenium content and reducing power. From analysis of several samples, an average reducing power of 0.025 milliequivalents corresponding to 2.33 mg. of rhenium was obtained. This corresponded to a mean oxidation state of +6 for the rhenium and indicated that some perrhenate was present in the solid mixture. Moreover, the experiments demonstrated that the rhenide compound was only slightly soluble in liquid ammonia and that this solvent was not suitable for extraction purposes.

The solvent action of anhydrous ethyl alcohol was then studied. The alcohol was introduced into the reaction chamber containing the sample. A stream of nitrogen served to stir the mixture and the alcohol was kept in contact with the solid for about one-half hour. The analysis of the dried alcohol extract showed that

both rhenide and potassium hydroxide had been extracted. In several instances, the solid in the reaction chamber was completely dissolved by the ethyl alcohol.

Dioxane, cellosolve, and n-amyl alcohol were then tested for their solvent action. Anhydrous dioxane proved unsuccessful as an extractant for it did not dissolve either component from the mixture. Treatment of the solid mixture with anhydrous cellosolve resulted in the removal of some potassium hydroxide and a considerable amount of rhenide. When n-amyl alcohol was used, the alcohol extract gave no test for rhenide with thallium(I) nitrate; the extract, however, contained a considerable quantity of potassium hydroxide. Inasmuch as the extract possessed high viscosity filtration was difficult and at times impossible. Therefore, n-butyl alcohol, a solvent of lower viscosity, was tested. The solid mixture was transferred from the reaction chamber into a 40 ml. glass stoppered centrifuge tube. The tube was filled with anhydrous n-butyl alcohol and shaken for an hour. After the resulting mixture was centrifuged, two layers of liquid were found. The upper clear alcohol layer gave no test for rhenide with thallium(I) nitrate, whereas the lower brown heavy layer had a high reducing power. Weighed amounts of the brown layer were analyzed for reducing power and rhenium content. Inasmuch as potassium dichromate oxidized some n-butyl alcohol in the

colored liquid being analyzed, standard iodine solution was used for titration. Typical analyses of the brown layer showed the presence of 1.1 to 1.5 per cent of rhenium, all essentially in rhenide form.

When this same procedure and technique were used with isopropyl alcohol as a solvent, the results obtained were similar. However, this new solvent offered some advantages over n-butyl alcohol: potassium hydroxide is more soluble in isopropyl alcohol than in the higher alcohol and the resulting alcoholic-potassium hydroxide extracts are much less viscous than those of n-butyl alcohol.

2. Extraction of potassium hydroxide by isopropyl alcohol. The following procedure was followed in the extractions employing isopropyl alcohol: One hundred milliliters of the 3 mM potassium perrhenate in ethylenediamine-water solution containing 9.8 per cent water was reduced at an initial temperature of about 25° C. by 4.00(±0.05) g. of Baker and Adamson potassium in the apparatus shown in Figure I. The solid product was twice washed with 100 ml. portions of anhydrous ethyl ether, being stirred at the same time. After a final rinse with another 100 ml. portion of the ether, the solid was dried thoroughly by means of a stream of dry oxygen-free nitrogen. The reaction chamber was removed from the assembly and immediately stoppered,

then transferred into a dry box containing phosphoric anhydride as desiccant. The dry box was provided with a dry oxygen-free nitrogen atmosphere (see p. 25). The solid was transferred to a 40 ml. glass stoppered centrifuge tube, and 30 ml. of the purified isopropyl alcohol (p. 9) was added to fill the tube. The tube was shaken for an hour on a shaking machine and then centrifuged for 2 minutes at 1000 rpm. A number of extractions of this solid with isopropyl alcohol resulted in the removal of a large proportion of the potassium hydroxide and in the eventual formation of two liquid layers.* The upper, colorless layer, formed in greater volume, contained much potassium hydroxide but no rhenide. The lower layer,brown in color and colloidal in nature,contained potassium hydroxide, isopropyl alcohol, and all of the rhenium, the latter apparently all in the uninegative state. Further extractions of the brown layer with isopropyl alcohol brought about the deposition of a solid and a diminution in the volume of the brown liquid. Continuation of the treatment until the brown layer had almost disappeared gave a grayish white solid containing in

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* Occasionally a small amount of white solid remained when the two layers were formed. The white solid was combined with the lower brown layer and the mixture further extracted as described for the brown layer alone.

TABLE IV

ANALYSIS OF SOLIDS PRODUCED

AFTER THE DISAPPEARANCE OF THE BROWN LAYER

Total rhenium, mg.	Per cent rhenium in solid	Rhenium titrated, mg.	Ml. 0.1 N $K_2Cr_2O_7$	Valence number change; theoretical, 8
32.30	52.9	16.15	6.78	7.82
31.80	29.4	15.90	6.87	8.05
31.60	20.9	15.80	6.91	8.15
17.35[a]	17.8	17.35	7.61	8.18

[a] This does not represent the total quantity of solid produced on extraction. In this case, a portion of the solid in the extraction tube was dumped directly into an excess of acidified standard dichromate for reducing power determination. After the titration the solution was made up to volume and an aliquot used for rhenium analysis. In all the other experiments the total solid in the tube was dissolved in 10 per cent potassium hydroxide solution and separate aliquots were withdrawn for reducing power measurement and rhenium determination.

most cases approximately 20 per cent rhenium, nearly all of which was apparently in the uninegative state. The results of typical experiments are given in Table IV.

The solid product obtained after the series of extractions with isopropyl alcohol was not sufficient in quantity to allow further study of the compound, so experiments were designed to produce larger quantities. The use of a specially designed Soxhlet extraction apparatus which could hold several batches of reduction product was unsuccessful. Extractions carried out with this apparatus, using a special glass thimble with a coarse sintered glass bottom, resulted in the formation of a heavy brown layer that passed through the porous glass. Furthermore, solids formed after hours of continuous extractions proved to contain considerable amounts of perrhenate. In other experiments a porous chromite thimble with glazed bottom was employed, but the heavy brown layer formed during the extraction accumulated in the pores of the chromite thimble and could not be recovered. When Soxhlet extraction had proved unsuccessful, the original mode of extraction (p. 32) was explored further.

In an effort to obtain maximum concentration of rhenide, the grayish white solid obtained from the brown layer was subjected to additional extractions

with isopropyl alcohol. In most of these experiments the solid became darker, and, although its rhenium content increased, the valence number change determined from the rhenium content and the reducing action toward dichromate was found to decrease somewhat, a fact which indicated that oxidation of part of the rhenium was occurring during extraction. This suggested that the brown liquid layer might contain some unreduced perrhenate, which appears in the grayish white solid material obtained by complete extraction of the brown layer, and, with decrease in the concentration of the hydroxide during further extraction of the solid, interacts with the rhenide to produce metallic rhenium. Therefore a series of fractional extractions of the brown liquid layer were carried out to test this hypothesis.

The following procedure was followed: Two reductions were carried out, each with 100 ml. of 3 mM potassium perrhenate solution in ethylenediamine-water mixture containing 10.8 per cent water; 6.00($\pm$0.05) g. of Baker and Adamson potassium was used as reducing agent and the reduction was carried out at an initial temperature of about 25° C. The white solid products from these two reductions were transferred in a dry box to a 60 ml. glass stoppered centrifuge tube. The tube was filled with purified isopropyl alcohol and then shaken in a mechanical shaker for one hour.

A total of three extractions usually resulted in the formation of the two layers described previously (see p. 32). The clear alcohol layer was drained off and the brown layer (plus any white solid which may have been present) was extracted once with isopropyl alcohol. Invariably there appeared at this stage a small amount of white solid. The clear alcohol layer was again drained off and the brown layer was separated from the solid by decantation to another 60 ml. glass stoppered centrifuge tube. The solid phase was extracted once again with the alcohol, and the rhenium content and reducing power determined. The results are given in the rows marked A in Table V. The brown liquid phase was subjected to three additional extractions with isopropyl alcohol, each of which gave a deposit of a gray solid. The small amount of the brown liquid still remaining was drained off, and the solid which had been deposited was extracted once more with the alcohol and analyzed. The results are given in the rows labeled B in the table. All manipulations involving exposure of the samples to the atmosphere were performed in the dry box.

The results shown in Table V are in agreement with the hypothesis that a small amount of unreduced perrhenate is present in the original brown liquid layer. The perrhenate is apparently thrown out with

TABLE V

FRACTIONAL EXTRACTION OF RHENIDE-POTASSIUM HYDROXIDE BROWN LIQUID PHASE[a]

Expt. no.		Weight of solid, mg.	Total rhenium content, mg.	Per cent rhenium	Valence no. change; theoretical, 8
1	A	22.7	11.7	51.5	3.85
	B	86.2	48.8	56.6	8.16
2	A	15.6	8.1	52.0	5.42
	B	157.1	70.5	44.8	7.72
3	A	18.7	8.5	45.4	6.56
	B	146.7	79.0	53.8	8.17
4	A	15.2	8.9	58.7	5.62
	B	162.7	76.0	46.8	8.14
5	A	39.9	7.9	19.7	6.16
	B	147.4	77.1	52.4	8.02
6	A	15.2	7.1	46.7	5.47
	B	190.9	85.3	44.7	8.00

[a] The original reductions were carried out at an initial temperature of about 25° C. with 100 ml. of 3 mM $KReO_4$ solution in ethylenediamine-water mixture containing 10.8 % water; 6.00(±0.05) g. of potassium was used as reducing agent. Each extraction experiment was performed on two batches of reduction product.

the first solid when the brown layer is treated with isopropyl alcohol.

A series of experiments was then performed to determine the maximum rhenide content obtainable in the solid. The gray solid material, which had been freed from perrhenate by the method just described, was further extracted with isopropyl alcohol until two successive extracts (each the product of one hour's treatment) gave no test for potassium hydroxide with phenolphthalein. The total number of extraction on the brown liquid layer freed from perrhenate averaged around 20. Starting with the fifth extraction, the solid was crushed with a glass rod prior to each addition of isopropyl alcohol. The solid was finally dissolved in 10 per cent potassium hydroxide solution and made up to a 100 ml. volume. Aliquot portions were then analyzed for rhenium content and reducing power. The data obtained from these experiments are given in Table VI. It is seen that the maximum rhenium content of the solid approximates 61 per cent. It should be pointed out that the solids analyzed still contained small amounts of potassium hydroxide, as evidenced by the fact that long contact (about 10 hours) with isopropyl alcohol resulted in the additional extraction of base.

TABLE VI

THE SEPARATION OF POTASSIUM RHENIDE FROM ADMIXTURE WITH POTASSIUM HYDROXIDE[a]

Expt. no.	Weight of solid, mg.	Total Re content, mg.	Per cent rhenium	Valence no. change; theoretical, 8
1	140.0	83.4	59.6	7.96
2	122.1	75.1	61.5	7.98
3	84.7	51.6	60.9	8.07
4	99.2	59.2	59.6	8.06
5	49.2[b]	26.9	54.6	8.14
6	102.4	54.2	52.9	8.10
7	102.6	55.4	54.0	8.21
8	41.0[b]	23.7	57.7	8.07

[a] The original reductions were carried out under the identical conditions described in Table V. Each extraction experiment was performed on two batches of reduction products.

[b] This does not represent the total quantity of solid obtained, a portion having been used for analysis for C, N, and H.

3. Analysis of the final product. Portions of two of the solids (see Table VI) were analyzed for carbon, nitrogen, and hydrogen. The results of these analyses are presented in Table VII.

TABLE VII

ANALYSIS OF RHENIDE COMPOUND FOR CARBON, NITROGEN, AND HYDROGEN

Analysts	Per cent C	Per cent N	Per cent H	H/Re atomic ratio	H_2O/Re molar ratio
Sample JB-1, experiment no. 5 Table VI, per cent Re=54.6					
Dr. G. Weiler and	0.54	0.82	2.14	7.3	3.6
Dr. F. B. Strauss	0.48	- - -	2.33	8.0	4.0
Microanalytical Laboratory 164 Banbury Road Oxford, England	Average of two analyses =			7.6	3.8
Sample JB-3, experiment no. 8 Table VI, per cent Re=57.7					
Micro-Tech Laboratories 8000 Lincoln Ave. Skokie, Illinois	0.10	0.45	2.50	8.0	4.0

Additional samples of the rhenide compound were prepared, extracted as previously described, and analyzed for both rhenium and potassium. From the excess of potassium beyond that required for potassium rhenide formation, the percentage of potassium hydroxide present as impurity was calculated; the water content was obtained as the difference between the total quantity of material and the sum of the potassium rhenide and potassium hydroxide present. The results, which are shown in Table VIII, also definitely indicate that potassium rhenide is formed as a tetrahydrate. The actual percentages of water and the water:rhenium ratios are a little lower than those which appear in the table, since the small and variable (ca. 1 to 2 per cent; see table VII) content of organic material, presumably ethylenediamine, has been neglected in the calculations.

TABLE VIII

ANALYSIS OF POTASSIUM RHENIDE[a]

Per cent rhenium	Calc'd per cent KRe	Per cent potassium	Calc'd per cent KOH	Per cent water	H_2O/Re molar ratio
58.4	70.7	17.8	7.9	21.4	3.8
55.8	67.5	16.6	7.0	25.5	4.7
57.2	69.2	15.6	5.1	25.6	4.6
57.9	70.1	15.5	4.8	25.1	4.5

[a] The product was washed with anhydrous ethyl ether and treated with a stream of dry oxygen-free nitrogen.

TABLE IX

TYPICAL CALCULATION OF WATER TO RHENIUM RATIO BASED UPON POTASSIUM AND RHENIUM ANALYSES

Sample no. 4 Table VIII

Per cent rhenium - - - - - - - - - 57.9 %

Per cent potassium - - - - - - - 15.5 %

Moles of rhenium/ g. of material = $\frac{0.579}{186.3}$ = 0.0031 moles

Moles of potassium/ g. of material - - - - - - - - - - = $\frac{0.155}{39.1}$ = 0.00396 moles

Per cent KRe - - - - - - - - - - = 57.9 x $\frac{225.4}{186.3}$ = 70.1 %

Per cent potassium required for KRe - - - - - - - - - = 70.1 x $\frac{39.1}{225.4}$ = 12.2 %

Excess per cent potassium - - - = 15.5 - 12.2 = 3.3 %

Per cent KOH corresponding to excess potassium - - - - - = 3.3 x $\frac{56}{39.1}$ = 4.8 %

Per cent water - - - - - - - - - = 100 - (70.1 + 4.8)

= 25.1 %

Moles of water/ g. of material- = $\frac{0.251}{18}$ = 0.01395 moles

H_2O to Re ratio - - - - - - - - - = $\frac{0.01395}{0.0031}$ = 4.5 moles

E. Magnetic Susceptibility Measurements.

In an effort to obtain information regarding the structure of the rhenide ion, magnetic studies on the gray solid were made. A Gouy type magnetic balance[20] was used for these experiments. Directions for the use of the balance and methods for calculating magnetic moments were found in works by Selwood[18] and by Weissberger,[19] as well as in a thesis by Thompson.[20]

The calculation of volume susceptibility was made by means of the following relationship:

$$\frac{(W_{30} - W_{10})(K_W - K_a)}{W_{20} - W_{10}} = K_x - K_a \text{ , where}$$

W_{10} = weight of the sample tube with current on minus weight with current off when the tube is filled with air.

W_{20} = the same difference for water.

W_{30} = the same difference for test material.

K_a = known volume susceptibility of air.

K_W = known volume susceptibility of water.

K_x = volume susceptibility of test material.

Since the coil current may vary slightly during the weighings, each change in weight must be corrected by a proportionality factor. The change in weight is proportional to the square of the coil current.

$$\frac{W_0}{W} = \frac{I_0^2}{I^2} \text{ ,}$$

where W is the weight change at a current I, and W_0 is the weight change corrected to a standard current I_0.

Division of the volume susceptibility by the apparent density of the test material gives the gram susceptibility. The Bohr magneton number, i. e., the effective magnetic moment, of a pure paramagnetic substance may then be calculated by the relationship

$$\mu_{eff.} = 2.84\sqrt{\chi_m T}$$

where χ_m is equal to the molar susceptibility of the substance and T the absolute temperature at which the measurement is made.

The Gouy balance has application as an analytical tool in the study of mixtures, or of compounds of known impurity. So long as no interaction occurs between the components of a mixture, the effective susceptibility of each component is proportional to the weight fraction of that component (Wiedemann's Additivity Law).[19] If one knows the composition of a binary mixture, one can calculate the magnetic susceptibility of a new compound from the resultant magnetic susceptibility and from the known magnetic susceptibility of the other component.

The susceptibility of Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, was determined in order to check the magnetic balance. An effective moment of 5.40 Bohr magnetons was obtained. This value is in excellent agreement with values of 5.25 and 5.46 reported in the literature,[81]

and with Thompson's value of 5.40.[80]

Potassium rhenide samples were prepared according to the procedure already described. The weighing tube (of 0.022 cm^2 cross section) was cleaned, dried, and placed in the dry box. The solid rhenide compound was introduced into the tube to the 7 cm. mark and the appropriate weighings were made.

The rhenide compound proved to be slightly paramagnetic. At 20° C., values of 254 x 10^{-6} and 223 x 10^{-6} c.g.s. unit, respectively, were obtained for the molar susceptibility of $KRe.4H_2O$ in two different samples, after correction for diamagnetism of the potassium hydroxide impurity. (Sample calculations are given in Table X.) This degree of paramagnetism is even less than that (ca. 1300. x 10^{-6} c.g.s. unit) required for a substance with one unpaired electron. Inasmuch as the rhenium atom possesses five unpaired electrons, the magnetic evidence indicates that the formation of the rhenide ion involves a considerable modification in electronic configuration.

There have been three suggestions in the literature regarding possible structures for the rhenide ion. Lingane[6] has suggested the following possible structures

A $5s^2 5p^6 5d^6 6s^2$

B $5s^2 5p^6 6s^2 6p^6$.

Pauling[8] has suggested the likelihood of the existence

TABLE X

SAMPLE DATA AND CALCULATIONS FOR

DETERMINING THE MAGNETIC SUSCEPTIBILITY OF

POTASSIUM RHENIDE TETRAHYDRATE

t = 20°C.

Cell empty

11.33361 g. (current off)
11.33320 g. (current = 4.57 amp.)
W_1 = -0.00041 g.
W_{1o} = -0.00041 g. (standard current = 4.57 amp.)

Cell with water

11.48986 g. (current off)
11.48910 g. (current = 4.55 amp.)
W_2 = -0.00076 g.
W_{2o} = -0.000766 g. (at standard current = 4.57 amp.)

Cell with potassium rhenide

11.48734 g. (current off)
11.48726 g. (current = 4.60 amp.)
W_3 = -0.00008 g.
W_{3o} = -0.000079 g. (at standard current = 4.57 amp.)

Calculation of field strength

$$H^2 = \frac{2 \times g (W_{2o} - W_{1o})}{A (K_w - K_a)}$$

$$= \frac{2 \times 980(-0.000766 + 0.00041)}{0.022(-0.72 \times 10^{-6} - 0.029 \times 10^{-6})}$$

H = 6510 gauss

TABLE X
(Continued)

Calculation of the susceptibility of the rhenide.

$$\frac{(W_{30} - W_{10})(K_w - K_a)}{(W_{20} - W_{10})} = K_x - K_a$$

$$\frac{(-0.000079 + 0.00041)(-0.72 \times 10^{-6} - 0.029 \times 10^{-6}}{(-0.000766 + 0.00041)} =$$

$K_x - 0.029 \times 10^{-6}$

$K_x = 0.723 \times 10^{-6}$ c.g.s. unit.

Volume of sample = 0.156 cc.

Weight of sample = 0.1415 g.

Apparent density = 0.93 g./cc.

χ_g (gram susceptibility of mixture) $= \frac{0.723 \times 10^{-6}}{0.93}$

$= 0.777 \times 10^{-6}$ c.g.s. unit.

Use of Wiedemann's Law

Per cent rhenium in sample - - - - - = 58.5 %

Calculated per cent $KRe.4H_2O$ - - - - = 93.37 %

Per cent potassium hydroxide - - - - = 6.63 %

χ_g for potassium hydroxide[22] - - - = -0.33×10^{-6} c.g.s. unit

$$\chi_g \text{ (mixture)} = \chi_g(KRe.4H_2O) \times 0.9337 + \chi_g(KOH) \times 0.0663$$

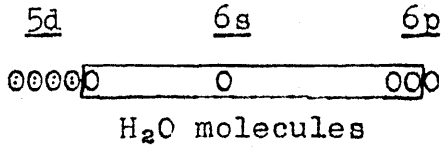
$\chi_g(KRe.4H_2O) = 0.856 \times 10^{-6}$ c.g.s. unit

Formula weight of $KRe.4H_2O$ = 297.4

χ_m(molar susceptibility) $= 297.4 \times 0.856 \times 10^{-6}$

$= 254 \times 10^{-6}$ c.g.s. unit.

of a tetrahydrate of a square planar structure, involving dsp^2 bonds.



Although the magnetic evidence definitely eliminates structure A above, it does not distinguish between the other two proposals.

F. Some Properties of Potassium Rhenide Tetrahydrate.

Although potassium rhenide tetrahydrate, as isolated, is gray in color, it is probable that the pure substance is actually colorless, inasmuch as the original reduction product, a mixture of potassium rhenide and potassium hydroxide, is colorless. The gray color appears after extraction from the brown, colloidal dispersion in isopropyl alcohol, and probably is attributable to the adsorption of colloidal material. That this is a reasonable explanation is seen from the fact that the compound dissolves in aqueous potassium hydroxide solution to give a pale yellow solution which exhibits the Tyndall effect. After several hours, the compound in the aqueous potassium hydroxide solution starts to decompose and form a brown precipitate. When, however, the compound is dissolved in distilled water, there can be clearly observed immediately after dissolution the evolution of gas due to the reaction of the compound with water, and a change in the color of the solution becomes very evident in a few minutes.

IV. SUMMARY

The reduction of potassium perrhenate in ethylenediamine-water solutions by means of potassium metal yields a white solid containing uninegative rhenium (rhenide) mixed with potassium hydroxide. Under optimum conditions of reduction a conversion of greater than 50 per cent of the perrhenate to solid rhenide is obtained.

A number of extractions of the solid with isopropyl alcohol results in the removal of a large proportion of the potassium hydroxide and in the eventual formation of a colloidal brown liquid which contains potassium hydroxide, isopropyl alcohol, and rhenium, the latter almost entirely in the uninegative state. Fractional extraction of this brown liquid finally gives a gray solid usually containing between 55 to 60 per cent rhenium, all as potassium rhenide.

Analysis of the gray solid shows the presence of small amounts (about 5 per cent) of potassium hydroxide as impurity and also the presence of approximately four molecules of water per rhenide ion. Magnetic measurements demonstrate that the rhenide compound is slightly paramagnetic, the degree of paramagnetism being even less than that required for a substance with one unpaired electron. Inasmuch as the rhenium atom possesses five unpaired electrons, the magnetic evidence indicates

that the formation of the rhenide ion involves a considerable modification in electronic configuration. The magnetic data do not distinguish between two alternative structures: one in which the rhenide ion has a halide configuration, and the other in which the rhenium exists in a hydrated complex having four molecules coordinated at the corners of a square.

V. SUGGESTIONS FOR FUTURE WORK.

Inasmuch as the structure of the uninegative rhenium compound could not definitely be elucidated by means of magnetic measurements, it would be of importance to make an X-ray study of the compound.

Relatively little information has been obtained regarding the chemical properties of the rhenide compound. It would be of interest to study the effect of air oxidation of the compound in basic and neutral aqueous solutions. The reaction with water alone should be investigated. Also, attempts should be made to remove the water of hydration under non-oxidizing conditions.

In view of the solubility of potassium perrhenate in liquid ammonia, reductions in this medium would be of interest. These reductions could be carried out by means of potassium alone, and also by potassium in the presence of ammonium salts.

Attempts should be made to study the reduction of solid potassium perrhenate at elevated temperature by means of both molecular and atomic hydrogen.

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